

# Manganese (II) –Selective Potentiometric Sensor Based on Calix[4]resorcinarene in PVC Matrix

M. Sobhana, T. Divya, E.V. Anuja, K. Girish Kumar\*

<sup>1</sup>Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682022, India

\*giri@cusat.ac.in; sobhanareji@gmail.com; divyathomas@cusat.ac.in; anujaev@cusat.ac.in

## Abstract

A new Manganese (II) PVC membrane sensor incorporating 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene (TNCR) as ionophore, tetraphenylborate (NaTPB) as anion excluder and dioctylphthalate (DOP) as plasticizer was constructed. The electrode exhibited an excellent potentiometric response over a wide concentration range of  $1.0 \times 10^{-5}$  -  $1.0 \times 10^{-1}$  M with a Nernstian slope of  $29.8 (\pm 0.4)$  mV decade<sup>-1</sup>. The detection limit was  $5.1 \times 10^{-6}$  M. The electrode showed a better performance over a pH range of 3.2 – 7.0, and had a short response time less than 25 s. The electrode was successfully applied for the potentiometric titration of Mn (II) against EDTA.

## Keywords

Calix[4]resorcinarene; Manganese (II); PVC Membrane; Potentiometry; Ion Selective Electrode

## Introduction

Manganese is an essential trace element for all living organisms and a part of many biological enzymes [Florence, 1982]. Human bodies contain about 10-20 mg of manganese, most of which is located in the kidneys and liver and it also functions as an enzyme activator and a component of metalloenzymes. Neanderthals has used black manganese dioxide as a cosmetic fifty thousand years ago [Henke et al, 2007]. Manganese is an essential micronutrient for all living organisms but it is highly toxic at higher concentration levels. Prolonged exposure to manganese dust and fumes may affect central nervous system. Symptoms of manganese poisoning are hallucinations, forgetfulness, lung embolism, bronchitis, headache and insomnia. A form of Parkinson's disease type neurodegeneration called 'Manganism' has been linked to high exposure to manganese dusts amongst miners and smelters since the early 19<sup>th</sup> century [Normandin et al., 2002]. The common methods adopted for the determination of manganese are AAS and ICP-MS [Cabrera-Vique et al., 2000, Sohrin et al., 2008]. But these techniques are

costly and require sample pre-treatment and infrastructure back up and hence being not convenient for routine analysis. Potentiometric sensors are better suited as they offer advantages such as high selectivity, sensitivity, good precision simplicity and low cost. Ion Selective electrodes are versatile devices with extraordinary analytical techniques [Sheikhshoaie et al, 2012]. Though the determination of manganese is important for both industrial and health purposes, only a few reports on manganese-selective electrodes are available in literature [Gholivand et al., 2009, Gupta et al., 2007, Mashhadizadeh et al., 2007, Midgley et al., 1985, Singh et al., 2005].

Macrocyclic compounds bearing appropriate binding groups act as efficient receptors for complexation of metal ions. Calixarenes are cavity-shaped cyclic oligomers made up of phenol units linked via alkylidene groups. Their configuration includes a number of selective factors, such as cavity-size, conformation and substituents, which leads to the formation of typical host-guest complexes with numerous compounds and allows for a variety of applications in ion-selective membranes and electrodes [Kivlehanaet al., 2007, Kumarb et al., 2009, Yang et al., 2001].

In continuation to our work on metal analysis at trace levels [Girishkumar et al., 2001, Girishkumar et al., 2006, Girishkumar et al., 2006, Girishkumar et al., 2007] a novel potentiometric sensor based on 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene (TNCR) as an electroactive material has been developed for the selective determination of Mn (II) ions. To the best of our knowledge, the application of TNCR as ionophore in membrane electrodes for the determination of Mn (II) ions has not been reported yet.

## Experimental

### Reagents and Materials

All the reagents used were of analytical reagent grade.

THF, dioctyl phthalate(DOP), dibutyl phthalate(DBP), dioctylsebacate(DOS), dioctyladipate (DOA), dimethyl sebacate (DMS), dibutylsebacate(DBS) and sodium tetraphenylborate (NaTPB) were obtained from Lancaster (UK) and used as received. The metal salts and high molecular weight PVC ( $M_w \sim 80,000$ ) were purchased from Merck and used without further purification. Ethylenediaminetetraacetic acid (EDTA), resorcinol, p-toluenesulphonic acid, 2-naphthaldehyde and other solvents were all of analar grade and procured from local vendors. Aqueous solutions were prepared in double distilled water. Solutions of different concentrations of manganese were prepared by serial dilution of 0.1M stock solution.

High molecular weight PVC ( $MW \sim 80,000$ ) was used for the preparation of membrane. PVC acts as the matrix of the membrane.

### Apparatus

All the potential measurements were carried out on a Metrohm 781 ion pH meter. The CHN analysis was performed using a CHN analyzer, ElementarVario. The UV-Visible spectra were recorded using Spectro UV-Visible Double Beam UVD-3500 instrument. FT-IR spectra were recorded on JASCO 4100 FT-IR spectrometer using KBr discs. SEM analysis was done on JOEL 6300 LV.  $^1H$  NMR spectra were recorded using JOEL GSX 400 NB FT NMR spectrometer.

### Synthesis of Ionophore

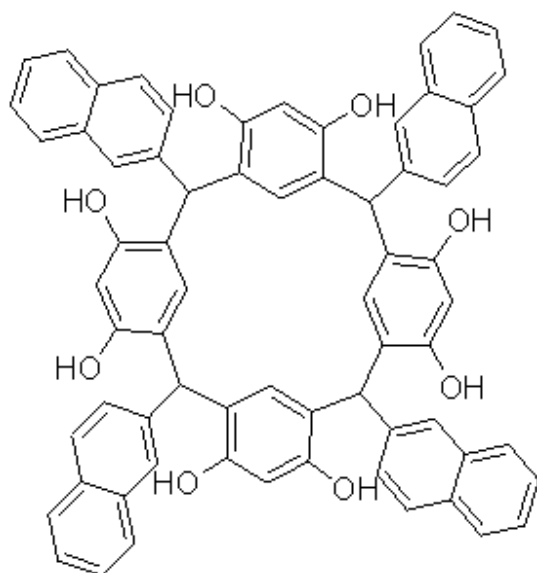


FIG. 1 STRUCTURE OF THE IONOPHORE

The ionophore, 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene was synthesized by the solvent free method [Roberts et al., 2001]. A 1:1 mixture of 2-naphthaldehyde and resorcinol (0.5 to 1.0 g scale)

along with a catalytic amount of p-toluenesulphonic acid (ca. 5%) were mixed together in a mortar and pestle, and ground vigorously. Within seconds, a viscous paste forms, this hardens on further grinding. The paste was left to stand for up to 1 hour, during which time it solidified. The solid was reground, washed with water to remove any acid, filtered and purified by column chromatography; then dried in vacuum. The structure of TNCR (FIG. 1) was confirmed by analytical and spectroscopic methods.

### Electrode Preparation

The PVC based membranes were prepared by dissolving appropriate amounts of the ionophore (TNCR), anion excluder NaTPB, plasticizer and PVC in minimum quantity of THF. This solution was stirred vigorously with a glass rod. When the solution became viscous, it was poured in acrylic rings glued on a smooth glass plate. The evaporation of the solvent has to be carefully controlled to obtain membranes of uniform morphology and thickness. The membranes, thus obtained were detached from glass plate, and cut to suitable size and glued to one end of a Pyrex glass tube. The electrode body was filled with  $1.0 \times 10^{-1}$  M  $MnCl_2$  solution and conditioned by dipping it in  $1.0 \times 10^{-1}$  M  $MnCl_2$  solution for 2 days. Membranes of different compositions were prepared and optimized so that the potentials recorded were reproducible and stable within the standard deviation.

### Equilibration of Membranes and Potential Measurements

The time required for complete equilibration and the concentration of the contacting solution was optimized by immersing all the membranes in  $MnCl_2$  solution of different concentrations for different time periods. Best results were obtained when the membranes were equilibrated for 2 days in  $1.0 \times 10^{-1}$  M  $MnCl_2$  solution. An Ag/AgCl was used as an internal reference electrode.

All potential measurements were carried out at  $(25 \pm 0.1)^\circ C$  using the following cell assembly Ag/AgCl (3.0M KCl)/0.1M  $MnCl_2$  Internal solution/PVC membrane/Test solution/ (3.0 M KCl) AgCl/Ag.

The performance of the developed Mn (II) sensor was investigated by measuring the potential of Mn (II) solutions prepared in the concentration range  $1.0 \times 10^{-1}$  –  $1.0 \times 10^{-8}$  M.

### Results and Discussions

The ionophore incorporated into the PVC matrix is the electroactive species that selectively binds to the

particular ion of interest. The potential response of the sensor based on TNCR has been tested for various cations. The selectivity of the proposed sensor for Mn (II) ions is demonstrated in FIG. 2. It was found that the membrane electrode responds to Mn (II) with a Nernstian slope while all other cations exhibit a sub-Nernstian slope.

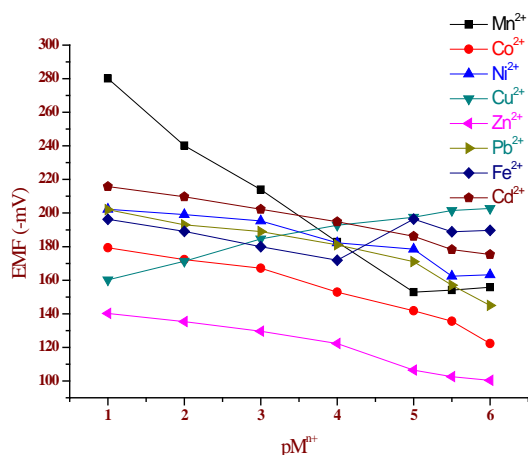


FIG. 2 POTENTIAL RESPONSE OF THE DEVELOPED SENSOR BASED ON TNCR TO DIFFERENT CATIONS

### Effect of Membrane Composition

The selectivity and sensitivity of the membrane depend not only on the nature of the ionophore used but also significantly on the membrane composition and the properties of plasticizers and additives used [Mashhadizadeh et al., 2002., Perez et al., 2003, Shamsipur et al., 2001]. The performance characteristics of several membranes having different composition are listed in Table 1. A regular support matrix for the membrane is provided by PVC. It was found that the sensor works well when the Plasticizer/PVC ratio is about 2, which ensures enough mobility of the membrane constituents. This is due to the fact that the dielectric constant of the membrane and the mobility of the ionophore molecules in the membrane is influenced by the nature of

plasticizer used [Yang et al., 1997]. Among the different plasticizers used, the membrane incorporating DOP gave the best results. The amount of ionophore is also found to affect the sensitivity of the PVC membrane. The optimum amount of the ionophore has been found to be 2.0 (%w/w). However, further increase in the amount of ionophore resulted in diminished calibration slope of the sensor. It may be due to certain inhomogeneities and saturation of the membrane [Bakker et al., 1997]. The additions of anionic excluders help to reduce the membrane resistance and improve the selectivity. The response of the sensor is based on a neutral carrier mechanism in which the ionophore exhibits strong affinity towards  $Mn^{2+}$  ions to form positively charged complexes in the membrane phase. Lipophilic anionic sites in the membrane stabilize these complexes [Kamel et al., 2010]. The anionic additives may also catalyze the exchange kinetics at the sample membrane interface [Gehrig et al., 1990].

Table 1 indicates that the best performance is observed when the membrane electrode composition is TNCR: PVC:DOP: NaTPB(w/w%) as 2 : 32 : 63 : 3 and it gives a Nernstian slope of  $29.8 (\pm 0.4)$  mV decade<sup>-1</sup>.

### Response and Life Time of the Sensor

Response time is the average time required for the manganese ion sensor to reach a potential within  $\pm 1$  mV of final equilibrium value. The practical response time of the sensor was calculated by measuring the time required to attain the equilibrium potential by dipping the sensor in a series of Mn (II) ion solutions each having a tenfold difference in concentration. The practical response time of sensor was found to be 25 s. The equilibrium potentials essentially remained constant for more than 5 min. The membrane sensor proposed could be used for at least 4 months without any measurable divergence in concentration range, slope and response time.

TABLE 1 OPTIMIZATION OF COMPOSITION OF THE SENSOR BASED ON TNCR

Sensor	w/w % composition of each membrane				Working concentration range (M)	Slope (mV decade <sup>-1</sup> )
	TNCR	PVC	Plasticizer	NaTPB		
1	2.0	95	0	3	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	$19.2 \pm 0.9$
2	1.0	32	DOP, 64.0	3	$5.0 \times 10^{-4} - 1.0 \times 10^{-1}$	$20.1 \pm 0.6$
3	1.2	32	DOP, 63.8	3	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$22.1 \pm 0.1$
4	1.6	32	DOP, 63.4	3	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	$23.2 \pm 0.6$
5	1.8	32	DOP, 63.2	3	$8.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$27.5 \pm 0.3$
6	2.0	32	DOP, 63	3	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$29.8 \pm 0.4$
7	3.0	32	DOP, 62.0	3	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$26.1 \pm 0.5$
8	2.0	32	DOA, 63.0	3	$5.0 \times 10^{-1} - 1.0 \times 10^{-1}$	$27.5 \pm 0.4$
9	2.0	32	DBP, 63.0	3	$5.0 \times 10^{-1} - 1.0 \times 10^{-1}$	$34.9 \pm 0.2$
10	2.0	32	DMS, 63.0	3	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	$22.1 \pm 0.9$
11	2.0	32	DOS, 63.0	3	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$	$25.9 \pm 0.7$
12	2.0	32	DBS, 63.0	3	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$	$32.9 \pm 0.8$

### Effect of pH and Non-aqueous Media

The influence of pH on the potential response of the sensor was studied in  $1.0 \times 10^{-3}$  M and  $1.0 \times 10^{-4}$  M solutions over a pH range of 2.0 – 9.0 (Fig. 3). The pH changes were induced through small additions of concentrated nitric acid (0.05 M) or sodium hydroxide (0.05 M). The electrode response is hardly affected by change in pH in the range of 3.2 – 7.0. The observed drift in potential at higher pH may be due to the formation of some hydroxyl complexes of Mn (II) ion in solution and at lower pH which is most probably due to the response of the sensor to  $H^+$  ions.

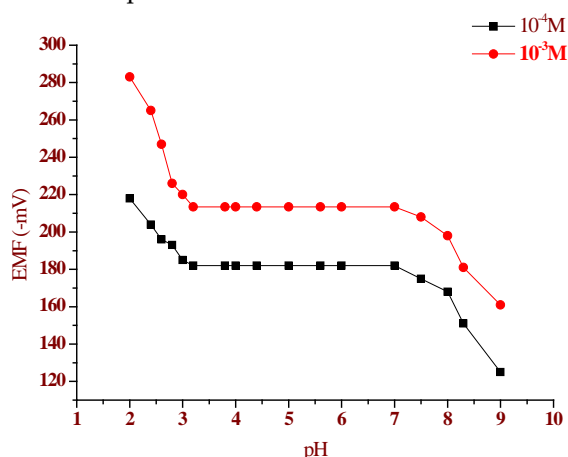


FIG. 3 EFFECT OF pH ON THE SENSOR BASED ON TNCR

TABLE 2 EFFECT OF PARTIALLY NON-AQUEOUS MEDIUM ON THE SLOPE AND WORKING CONCENTRATION RANGE OF THE SENSOR

Non-aqueous content(%v/v)	Slope (mV decade <sup>-1</sup> )	Working concentration range(M)
0	29.8	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
Ethanol		
10	29.6	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
20	30.3	$2.6 \times 10^{-5}$ – $1.0 \times 10^{-1}$
25	28.2	$5.8 \times 10^{-5}$ – $1.0 \times 10^{-1}$
30	21.3	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-1}$
Methanol		
10	29.3	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
20	30.2	$3.4 \times 10^{-5}$ – $1.0 \times 10^{-1}$
25	28.3	$7.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
30	21.4	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-1}$

The functioning of the sensor in partially non-aqueous media was also investigated using ethanol-water and methanol-water mixtures and the results are presented in Table 2. The membranes do not show any appreciable change in working concentration range or slope in mixtures up to 25% (v/v) non-aqueous contents and hence the electrode can be satisfactorily used in mixtures containing up to 25% non-aqueous content. Above this level, the slope gets affected, which may be due to leaching of the ligand into the sample solution.

### Calibration Curve

The proposed membrane electrode was examined with different concentrations of the inner reference solution from  $1.0 \times 10^{-5}$  –  $1.0 \times 10^{-1}$  M. A  $1.0 \times 10^{-1}$  M concentration of the reference solution is quite appropriate for smooth functioning of the membrane electrode system. The optimum equilibration time for the membrane electrode in the presence of  $1.0 \times 10^{-1}$  M  $MnCl_2$ , was 48 h, after which it would generate stable potentials in contact with the manganese solution. The electrode showed a linear response in the range  $1.0 \times 10^{-5}$ –  $1.0 \times 10^{-1}$  M at 25°C (FIG. 4). The slope of the calibration graph was  $29.8 (\pm 0.4)$  mV decade<sup>-1</sup>. The limit of detection was  $5.1 \times 10^{-6}$  M, derived from the intersection of the extrapolated segments of the response potential of  $Mn^{2+}$ .

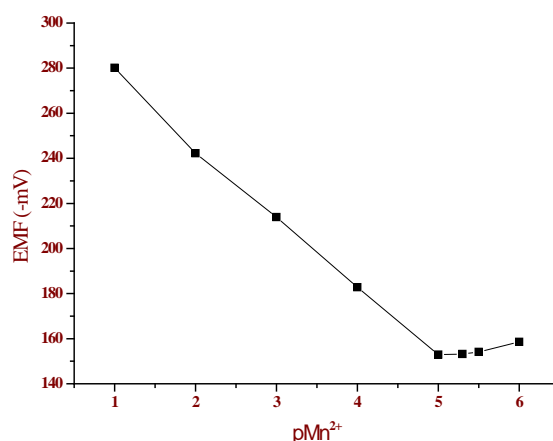


FIG. 4 CALIBRATION GRAPH OF THE SENSOR BASED ON TNCR

### Potentiometric Selectivity

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}} \quad (1)$$

The response of any ion selective sensor to the primary ion in the presence of other ions present in the solution is expressed in terms of the potentiometric selectivity coefficient. The interference of various ions on the selectivity of the developed sensor has been examined by the Fixed Interference Method [Bakker et al., 2000, Buck et al., 1994]. The selectivity coefficients were determined at  $1.0 \times 10^{-2}$  M concentration of foreign ions. The concentration of Mn (II) was varied and the selectivity coefficient was calculated using equation:

The selectivity coefficient values are shown in Table 3. The selectivity coefficient was determined by the Fixed Interference Method. When Mn(II) alone was used, the selectivity coefficient was found to be 1, hence not shown in Table 3. Of course, that is the usual practice. The selectivity coefficient was determined by mixing Mn (II) with other metal ions like  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Sn^{2+}$  etc as

shown in Table 3. And the results showed that the selectivity for other metal ions is negligible in presence of Mn (II) ions. The values indicate that the developed sensor exhibits the highest selectivity for Mn (II) ions over a number of cations.

TABLE 3 SELECTIVITY COEFFICIENTS FOR THE SENSOR USING FIXED INTERFERENCE METHOD AT  $1.0 \times 10^{-2}$  M CONCENTRATION OF INTERFERING ION

Interfering ion (X)	Selectivity Coefficient
$\text{Cd}^{2+}$	$8.6 \times 10^{-4}$
$\text{Co}^{2+}$	$4.1 \times 10^{-3}$
$\text{Sn}^{2+}$	$5.6 \times 10^{-3}$
$\text{Cu}^{2+}$	$7.5 \times 10^{-3}$
$\text{Zn}^{2+}$	$4.4 \times 10^{-3}$
$\text{Pb}^{2+}$	$6.2 \times 10^{-3}$
$\text{Hg}^{2+}$	$2.7 \times 10^{-3}$
$\text{Fe}^{2+}$	$6.9 \times 10^{-4}$
$\text{Na}^+$	$8.1 \times 10^{-4}$
$\text{K}^+$	$9.3 \times 10^{-4}$
$\text{Ag}^+$	$5.6 \times 10^{-2}$
$\text{Ni}^{2+}$	$2.1 \times 10^{-1}$
$\text{Ca}^{2+}$	$2.8 \times 10^{-3}$
$\text{Cr}^{3+}$	$6.5 \times 10^{-3}$
$\text{Ba}^{2+}$	$3.8 \times 10^{-3}$

### Analytical Application

The developed Mn (II) sensor was also successfully applied as an indicator electrode in conjunction with Ag/AgCl electrode in the potentiometric titration of Mn (II) solution with EDTA. The titration plots obtained were all of a near sigmoid shape and the end point corresponds to 1:1 stoichiometry of Mn-EDTA complex (FIG. 5)

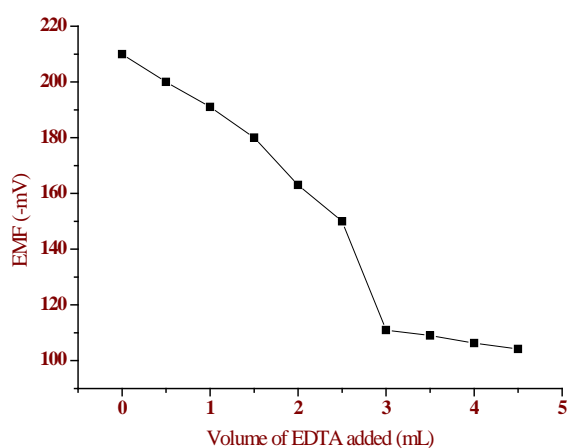


FIG. 5 POTENTIOMETRIC TITRATION CURVE OF 25.0 ML OF  $1.0 \times 10^{-3}$  M MN (II) SOLUTION WITH  $1.0 \times 10^{-2}$  M EDTA USING THE SENSOR BASED ON TNCR

The proposed sensor is comparable with the existing sensors in terms of response time, life time, slope, pH range and concentration range (Table. 4).

TABLE 4 A COMPARATIVE STUDY OF THE CHARACTERISTICS OF THE DEVELOPED SENSOR FOR Mn (II) WITH SOME REPORTED SENSORS

No	Working concentration range(M)	pH range	Life Time	Slope (mV decade <sup>-1</sup> )	Reference
1	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	4.0 - 8.0	3 months	$29.6 \pm 0.5$	Gupta et al., 2010
2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	4.0 - 9.0	2 months	$29.3 \pm 0.5$	Zawari et al., 2009
3	$1.2 \times 10^{-5} - 1.0 \times 10^{-1}$	3.0 - 8.0	4 months	$28.5 \pm 0.3$	Singh et al., 2005
4	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	NM	NM*	Non Nernstian	Hirata et al., 1972
5	$5.0 \times 10^{-5} - 1.0 \times 10^{-3}$	4.0	2 weeks	Near Nernstian	Midgley et al., 1985
6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.0 - 6.5	NM	$30.0 \pm 0.3$	Gupta et al., 2007
7	$4.0 \times 10^{-7} - 1.8 \times 10^{-2}$	4.5-7.5	2 months	$30.1 \pm 1.0$	Mashhadizadeh et al, 2007
8	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	3.2 - 7.0	4 months	$29.8 \pm 0.4$	Developed sensor

\*NM – not mentioned

### Conclusions

The use of 2,8,14,20-tetrakis(naphthyl)calix[4]resorcinarene as ionophore in potentiometric sensor enables the determination of manganese. The developed sensor exhibits a Nernstian response of  $29.8 (\pm 0.4)$  mV decade<sup>-1</sup> and its working concentration range was found to be  $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$  M with a detection limit of  $5.1 \times 10^{-6}$  M. The working pH range of the sensor was 3.2–7.0. The sensor has a fast response time and a long life time. The sensor can be successfully applied to the determination of  $\text{Mn}^{2+}$  ion by direct potentiometry against EDTA.

### ACKNOWLEDGEMENT

The authors acknowledge the financial support from Kerala State Council for Science Technology Environment (KSCSTE), Govt of Kerala, by means of a project.

### REFERENCES

- Bakker, E., P. Buhlmann, E. Pretsch, "Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics", Chemical Reviews 97 (1997): 3083-3132.
- Bakker, E., P. Buhlmann, E. Pretsch, "Selectivity of Potentiometric Ion Sensors", Analytical Chemistry 72 (2000): 1127-1133.
- Buck, R. P., E. Lindner, "Recommendations for Nomenclature of Ion-Selective Electrodes", Pure and Applied Chemistry 66 (1994): 2527-2536.

- Florence, T.M., "The Speciation of Trace Elements in Waters", *Talanta* 29 (1982): 345-364.
- Gehrig, P. M., W. E. Morf, M. Weltic, E. Pretsch, W. Simon, "Catalysis of Ion Transfer by Tetraphenylborates in Neutral Carrier-Based Ion-Selective Electrodes", *Helvetica Chimica Acta* 73 (1990): 203-212.
- Gholivand, M. B., M. Gorji, M. Joshaghani, "Manganese(II)-Ion-Selective Electrode Based on 2,2'-bis (salicylideneamino) Azobenzene Incorporated in Poly(Vinyl Chloride) Matrix", *Collection. Czechoslovak Chemical Communications* 74 (2009):1411-1424.
- Girishkumar, K., R. Muthuselvi, "Spectrophotometric Method for the Determination of Cobalt with N,N'-bis (2-aminobenzoyl) Ethylenediamine", *Microchimica Acta* 137 (2001): 25-28.
- Girishkumar, K., R. Muthuselvi, "Spectrophotometric Determination of Chromium(III) with 2-hydroxybenzaldiminoglycine", *Journal of Analytical Chemistry* 61 (2006):28-31.
- Girishkumar, K., R. Poduval, P. Augustine, S. John, B. Saraswathyamma, "A PVC Plasticized Sensor for Ni(II) Ion Based on a Simple Ethylenediamine Derivative", *Analytical Sciences* 22 (2006): 1333-1337.
- Girishkumar, K., R. Poduval, S. John, P. Augustine, "A PVC plasticized membrane for nickel ions", *Microchimica Acta* 156 (2007): 283-287.
- Gupta, V. K., A. K. Jain, G. Maheshwari, "Manganese (II) Selective PVC Based Membrane Sensor Using a Schiff Base", *Talanta* 72 (2007): 49- 53.
- Gupta, V. K., R. Jain, M. K. Pal, "Mn<sup>2+</sup> Selective Electrode Based on 3-(6-Aminopyridin-2-Ylimino)-1, 3-Diphenylpropylidene) Pyridine-2, 6-Diamine", *International Journal of Electrochemical Science* 5 (2010): 1164-1178.
- Henke, W., T. Hardt, *Handbook of Paleoanthropology*, 1 (2007): 1733-1734.
- Hirata, H., K. Higashiyama, "Ion Selective Chalcogenide Electrodes for a Nurser of Cations", *Talanta* 19 (1972): 391-398.
- Kamel, A. H., W. H. Mahmoud, M. S. Mostafa, "Response Characteristics of Copper-Selective Polymer Membrane Electrodes Based on a Newly Synthesized Macrocyclic Calix[4]arene Derivative as a Neutral Carrier Ionophore", *Electroanalysis* 22 (2010): 2453-2459.
- Kivlehana, F., W. J. Macea, H. A. Moynihanb, D. W. M. Arrigana, "Potentiometric Evaluation of Calix[4]Arene Anion Receptors in Membrane Electrodes: Phosphate Detection", *Analytica Chimica Acta* 585 (2007): 154-160.
- Kumarb, P., Y.B. Shima, "A Novel Cobalt(II)-selective Potentiometric Sensor Based on p-(4-n-butylphenylazo) calix[4]arene" *Talanta* 77 (2009): 1057-1062.
- Mashhadizadeh, M. H., A. Mostafavi, R. Razavi, M. Shamsipur, "Highly Selective Cu(II) PVC Membrane Electrode Based on 3,6,9,14- Tetrathiabicyclo[9.2.9.1] Tetradeca-11,13-diene as a Suitable Neutral Ionophore", *Sens. Actuators B* 86 (2002): 222-228.
- Mashhadizadeh, M.H., E. P. Taheri, I. Sheikhshoae, "A Novel Mn<sup>2+</sup> PVC Membrane Electrode Based on a Recently Synthesized Schiff Base", *Talanta* 72 (2007): 1088- 1092.
- Midgley, D., D. E. Mulachy, the Manganese (IV) Oxide Electrode as a Manganese(II) Sensor", *Talanta* 32 (1985): 7- 10.
- Normandin, L., A. S. Hazell, "Manganese Neurotoxicity: An Update of Pathophysiologic Mechanisms Metabolic Brain Disease", *Metabolic Brain Disease* 17 (2002): 375-386.
- Perez, M. D. A., L. P. Martin, J. C. Quintana, M. Yazdani-Perdram, "Influence of Different Plasticizers on the Response of Chemical Sensors Based on Polymeric Membranes for Nitrate Ion Determination", *Sens. Actuators B* 89 (2003): 262-268.
- Roberts, B. A., W. V. C. Gareth, C. L. Raston, J. L. Scott, "Solvent-free Synthesis of Calix[4]resorcinarenes", *Green Chemistry* 3 (2001): 280-284.
- Shamsipur, M., M. Javanbakht, M.F Mousavi, M. R. Ganjali, V. Lippois, A. Garau, L. Tei, "Copper(II)-selective Membrane Electrodes Based on Some Recently Synthesized Mixed Aza-thioether Crowns Containing a 1,10-phenanthroline sub-unit", *Talanta* 55 (2001): 1047-1054.
- Sheikhshoae, I., T. Shamspur, A. Mostafavi, S. Y. Ebrahimipur, "PVC-Membrane potentiometric Sensors Based on a Recently Synthesized Schiff Base for Fe(III) ion", *Bulletin of Chemical Society of Ethiopia* 26 (2012): 65-72.
- Singh, A. K., P. Saxena, A. Panwar, "Manganese (II)-selective PVC Membrane Electrode Based on a Pentaazamacrocyclic Manganese Complex", *Sensors and Actuators B* 110 (2005): 377-381.

Sohrin, Y., S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye, S. Umetani, "Multielemental Determination of GEOTRACES Key Trace Metals in Seawater by ICPMS after Preconcentration Using an Ethylenediaminetriacetic Acid Chelating Resin", *Analytical Chemistry* 80 (2008): 6267-6273.

Yang, X., N. Kumar, H. Chi, D. B. Hibbert, P. N. W. Alexander, "Lead-selective Membrane Electrodes Based on Dithiophenediazacrownether Derivatives", *Electroanalysis* 9 (1997): 549-553.

Yang, L., Y. He, W. Gan, M. Li, Q. Qu, X. Lin, "Determination of Chromium(VI) and Lead(II) in Drinking Water by Electrokinetic flow Analysis System and Graphite Furnace Atomic Absorption Spectrometry", *Talanta* 55 (2001): 271-279.

Zawari, M., M.Giahi, and H. Aghaie, "Manganese (II)-Selective PVC Membrane Electrode Based on N-(2-picolinamido Ethyl)-Picolinamide as ionophore", *Journal of Physical and Theoretical Chemistry* 5 (2009): 203-208.

**Girish Kumar**, born in 1962, obtained his M.Sc., degree and Ph.D in Chemistry from University of Kerala. He is working as a Professor of Analytical Chemistry at Dept. of Applied Chemistry, Cochin University of Science and Technology, Kochi. He is a visiting professor at Sultan Qaboos University, Muscat, Sultanate of Oman.

His main research interests are in the areas of chemical and electrochemical sensors for pharmaceutical applications, development of new methods for spectrophotometry and trace metal analysis, synthesis, characterization and application studies of coordination complexes including polymeric complexes, environmental chemistry and pollution monitoring. He has published over 70 articles in national and international journals and has presented about 95 papers in various seminars/symposia including invited talks. He has research collaboration with CECRI(CSIR),

Karaikudi, Tamilnadu; Department of Chemistry, IIT Roorke; and Department of Biosensors, Polish Academy of Sciences, Poland.

Dr. Kumar is a fellow member of the Indian Chemical Society; Member, Managing committee, Indian Society for Electro Analytical Chemistry (ISEAC); Member, Governing Council, Inter University Centre for Nano Materials and Devices, CUSAT; Member, Advisory Committee, Centre for Science in Society; Chairman, Board of Studies in Chemistry etc. He is a peer reviewer for many national and international journals such as *Talanta*, *Bioresource Technology*, *Applied Organometallic Chemistry*, *Journal of Applied Polymer Science*, *International Journal of Environmental Analytical Chemistry*, *Journal of Solid State Electrochemistry*, *Sensor Letters*, *Drug Testing and Analysis*, *Monatshefte für Chemie*, *Indian Journal of Chemistry*, *Indian Journal of Chemical Technology* etc. He has supervised 15 Ph.Dthesis and 9 M.phil thesis.

**Sobhana** has pursued her Master's degree in chemistry from Mahatma Gandhi University and Ph. D in Chemistry from Cochin University of Science and Technology, India. She is working as an Associate Professor in the Department of Chemistry, Maharajas College, Kerala, India.

**Divya** has received her M.Sc. degree in Chemistry from the University of Mysore in 2005 and M.phil (Chemistry) from University of Mysore in 2007. In 2009 she joined the Department of Applied Chemistry, Cochin University of Science and Technology, India as a graduate student and until now she is working on her thesis on development of electrochemical sensors. She has published three research articles in international journals and has presented several papers in national/ International conferences.

**Anuja** was born in Kerala, India on May 18; 1987. She received her Master's degree in chemistry from University of Calicut, India, in 2009. She joined the electrochemical sensor group, Department of Applied Chemistry, Cochin University of Science and Technology in 2011 and actively engaged in the development of electrochemical/fluorescent sensors for bio-active reagents, food additives etc. She has published research articles in international journal and presented papers in national/international conferences.